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(54) Title: METHOD OF CEMENTING A WELL

(57) Abstract

A method of cementing a well comprising preparing a mud-cement by admixing (a) a drilling mud, and (b) blast furnace slag and/or particulate glass; displacing the mud-cement to a preselected location in the well; and allowing the mud-cement to harden and set up.

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METHOD OF CEMENTING A WELL

The present invention relates to improvements in drilling mud-cement compositions for cementing oil and gas wells. The compositions are characterized by improved setting at low temperatures and resistance to strength retrogression at temperatures above 230-250 °F.

The general procedure of drilling an oil or gas well includes drilling a borehole using a drilling mud. Subsequent to drilling the borehole, casing is run into the well preparatory to placing a cement slurry in the annulus between the outside of the casing and the borehole wall. Wells with temperatures above 230-250 °F present special cementing problems.

For example, converted drilling fluid compositions using a C-Mix suggested in U.S. patent specification No. 3 499 491 are particularly temperature sensitive. In other words, if wellbore temperatures exceed 230-250 °F, the cement compositions or any converted drilling fluids suggested in U.S. patent specifications No 4 883 125 and No. 4 176 720 have a tendency to undergo thermal strength retrogression. Since the cement composition contains a substantial amount of Portland cement, the set cement composition has a tendency to undergo strength retrogression at temperatures above approximately 230-250 °F.

In the specification and in the claims the term "C-Mix" is used to designate a mixture of 20 to 60 wt% Portland cement, 10 to 50 wt% fly ash, 0 to 15 wt% soda ash, 0 to 50 wt% natural pozzolana, and 5 to 30 wt% powdered sodium silicate glass.

Thermal strength retrogression is a particular problem in cementing any deep, hot wells or wells associated with thermal recovery processes. For example, the Belridge field in California has two major producing zones, the Tulare Sands and the Diatomite/Brown Shale. The Tulare zone has been extensively steam flooded for several years such that temperatures in producing

intervals range from 250 °F to 400 °F. The Diatomite/Brown Shale formation lies beneath the Tulare Sands and extends from 700 feet to 4 000 feet. Since C-Mix undergoes severe strength retrogression at temperatures 230-250 °F, it cannot be used in cementing wells in this field.

Wells with low bottom hole temperatures also present special cementing problems. For example, wells in the North Hobbs field, New Mexico, have low bottom hole temperatures, e.g., approximately 100 °F at a depth of 4 000 feet. In addition, these wells are normally drilled with 10.5 lb/gal salt saturated muds. A low temperature, salt tolerant mud-cement formulation is needed to cement these wells. Another example for low temperature wells are those deep-water wells in the Gulf of Mexico. Mud-lime temperatures range between 40 °F and 60 °F. Surface casing cements for these wells must be activated at low temperatures.

Accordingly, the present invention is directed to overcoming the above-noted problems in the art and provides a solution as more particularly described hereinafter.

It is the primary purpose of the present invention to provide drilling mud-cement compositions which, after setting up in an oil or gas well, are suitable for cementing wells with a wide temperature range; e.g., 40-600°F.

To this end the method of cementing a well according to the present invention comprises

preparing a mud-cement by admixing (a) a drilling mud, and (b) blast furnace slag and/or particulate glass;

displacing the mud-cement to a preselected location in the well; and

allowing the mud-cement to harden and set up.

In a further embodiment of the invention the method further comprises admixing to the drilling mud a C-Mix, the amount of C-Mix being between 40 and 90 %wt of the total amount of blast furnace slag, powdered glass and C-Mix.

In the specification the term "S-Mix" will be used to designate a formulation prepared by adding about 100 wt% blast

furnace slag (basis S-Mix) to a water-base mud and one or more alkaline or other activating agents. S-Mix is designed to use for cementing wells with wide temperatures ranging from approximately 40 °F to 600 °F.

Blast furnace slag is a by-product of the iron ore refining process. Only quenched slag known as granulated, pelletized or rapid air blown slag has high hydraulic properties and is useful for this invention. Chemical activation of slag is entirely different from Portland cement. With Portland cement, upon addition of water, hydration of the cement begins. Slag will not react in water at moderate temperatures, but when chemically activated, hydration of slag will continue to set hard.

An alternative to the use of blast furnace slag is particulate glass, e.g., ground glass (ground to pass 325 mesh) or powdered glass. Glass is an amorphous, super cooled liquid material comprising silica, soda ash, and lime, that is practically inert to all chemicals. It is theorized, although the present invention is not limited to this theory, that the high surface area of ground glass can be a source of reactive sodium silicate at elevated temperatures, and especially in a high pH environment. In the specification and in the claims the expression "powdered glass" will be used to designate particulate glass, ground glass or powdered glass.

In the specification the term "HTC-Mix" will be used to a high temperature version of C-Mix, is prepared by adding 40 to 90 %wt of C-Mix (basis HTC-Mix which is the total amount of blast furnace slag, powdered glass and C-Mix) to blast furnace slag, or powdered glass, or to a mixture of blast furnace slag and powdered glass.

Other purposes, distinctions over the art, advantages and features of the invention will be apparent to one skilled in the art upon review of the following.

Slurries of C-Mix achieve high compressive strength on hardening, provide excellent rheology, and have zero-free water, low fluid loss, acceptable thickening times, and very low permeability. However, a problem with C-Mix is its thermal stability at

high temperatures. C-Mix slurries, which contain Portland cement only and non-hydraulic mud materials such as bentonite and low-gravity solids, show strength retrogression at temperatures above 230-250 °F (see Table 1).

TABLE 1 The effect of temperature and C-Mix concentration on compressive strength of C-Mix prepared with a 12 lb/gal seawater lignosulphonate mud.

C-Mix Conc.	200 lb/bbl		250 lb/bbl		300 lb/bbl	
Device Used	UCA*	API	UCA	API	UCA	API
Temperature	Compressive Strength (psi)					
140 °F	1 420	-	1 880	2 930	-	-
180 °F	1 150	1 500	1 640	2 370	-	-
220 °F	1 040	1 280	1 480	2 880	1 920	2 830
260 °F	690	-	360	260	710	510
300 °F	110	150	280	310	490	430

*UCA - Ultrasonic Cement Analyzer by Halliburton

Strength retrogression is primarily due to the breakdown of hydration products of Portland cement. Retrogression is amplified by the higher water content of C-Mix slurries in the presence of non-hydraulic materials in the mud.

In accordance with the present invention it has been discovered that admixing with a drilling mud blast furnace slag and/or powdered glass (S-Mix) and additionally C-Mix (HTC-Mix) produces new cementing materials which are resistant to thermal strength retrogression at temperatures up to and exceeding 450 °F, and which have major benefits including low slurry density, thixotropic nature, reduction of mud disposal volumes, simple operation, low cost, good rheology, zero-free water, low fluid loss, low permeability. high tolerance to contamination, and high compressive strengths.

An improved mud conversion process has been invented by adding blast furnace or particulate glass slag and one or more activating agents to drilling mud. Cementing with S-Mix does not require dry blending of materials if a composition with 100% slag is utilized. S-Mix jobs can be run using rig equipment without using cement pumping units. Bulk or sacked slag or glass can be added to the mud through the rig mud material mixing units. Dry or liquid chemical activators can be metered into the stream of mud. Bulk cement service and pumping charges can be reduced or eliminated since cementing operations are handled with the rig equipment if S-Mix is mixed with 100% slag.

In general, both batch mixing and continuous mixing are suitable for large volume HTC-Mix or S-Mix operations.

The present invention is most useful with the following water-base drilling muds: spud muds, seawater muds, salt water muds, brine muds, lime muds, gypsum muds, lignosulphonate muds, polymer (such as PHPA which is partially hydrolyzed polyacrylamide) muds, KCl inhibited muds, emulsion (oil in water) muds, surfactant muds, etc. This invention is expected to be applicable in all water-based fluids. Some hydrocarbons such as diesel, mineral oil or crude oil, or polyalcohol-type fluids can be tolerated in this invention.

S-Mix can be prepared by adding 100 wt% blast furnace slag to a water-base mud and one or more alkaline or other activating agents such as sodium sulphate. For example, although an S-Mix composition may have 75% slag, 25% Portland cement, and small amounts of activators, the composition with 100% slag is preferred over the former. Suitable activators for S-Mix include sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium sulphate, sodium silicates, and other alkaline materials.

A suitable activator for the HTC-Mix is sodium silicate; other suitable activators include fluorides such as sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, and alkaline material such as sodium carbonate, potassium

carbonate, sodium hydroxide, potassium hydroxide, and calcium hydroxide. The cement may be either a construction-grade cement or any API specified Portland cement.

Both HTC-Mix and S-Mix slurries are prepared by adding a dispersant (thinner and retarder) and HTC-Mix or S-Mix materials in a water-base drilling fluid. Of course, amounts of HTC-Mix or S-Mix determine slurry density, compressive strength and yield (volume increase). The specific dispersant(s) needed and the amount(s) required should then be determined. Rheological properties and cement slurry properties such as thickening time, free water, fluid loss, settling, etc.may also be determined by the dispersant(s).

The strength development of HTC-Mix or S-Mix slurries is heavily influenced by their concentrations in the mud and by the thinner or dispersants used. The type of thinner and its concentration are major variables that influence strength development. Thinners are also employed to control viscosity, thickening time, and setting time of the HTC-Mix or S-Mix. Three commercial thinners have been found to be especially beneficial for the HTC-Mix or S-Mix: 1) chrome-free sugar-containing lignosulphonates; 2) chrome-free de-sugared lignosulphonate; and 3) chrome-free sulfomethylated tree bark extract (a modified humic acid). About two to eight lb/bbl of such thinners is usually acceptable, although 15 to 20 lb/bbl can be used. Chrome-free sugar-containing lignosulphonate is a powerful retarder for both HTC-Mix and S-Mix. The retarding effect of chrome-free de-sugared lignosulphonate is moderate; chrome-free sulfomethylated tree bark extract may be used alone or added to chrome-free de-sugared lignosulphonate to produce a more efficient retarder and at the same time control rheology of the HTC-Mix or S-Mix slurry.

For example, lignosulphonate dispersants may not be desirable for non-dispersed polymer muds since the lignosulphonate have a tendency to promote dispersion of drill cuttings. Polymeric dispersants such as "CYPAN" (high molecular weight sodium polyacrylate by American Cyanamid), "NEWTHIN" (low molecular sodium polyacrylate from Milpark), and "MILTEMP" (sulphonated styrene maleic anhydride

from Milpark) are very effective in thinning and retarding the HTC-Mix or S-Mix slurries. Where formation conditions dictate, a non-dispersed system can easily be converted to a dispersed system to tolerate a higher degree of drilled solids. This can be done by adding lignosulphonate dispersants to the system.

HTC-Mix or S-Mix formulated with slag, e.g., blast furnace slag (tradename "NEWCEM" by Atlantic Cement Company and Colton slag from California Portland Cement Company), or particulate glass, e.g., ground or powdered glass, can set up at low temperatures (e.g., 40°F) and yet resist strength retrogression at temperatures of up to approximately 600 °F and higher, depending upon the specific formulation of the HTC-Mix and S-Mix and other conditions.

Conventional slag cements (mixtures of slag and Portland cement in water) have many useful properties directly or indirectly related with this invention. Slag cements resist degradation by acidic gases such as carbon dioxide and hydrogen sulphide, acids, sulphate water, and have demonstrated higher compressive strength than Portland cement. Slag cements produce a slurry that is lighter than Portland cements since its density is lower than Portland cement (specific gravity 2.90 vs. 3.14). Most importantly, properly formulated slag cements are thermally stable to 1 500°F and have a lower heat of hydration. The slag cements harden below its freezing point. In general, a small increase in temperature can cause a substantial increase of compressive strength.

The invention will now be described in more detail by way of example with reference to the examples.

The first examples relate to laboratory testing of HTC-Mix. Table 2 lists several suitable HTC-Mix formulations and their compressive strengths measured after aging at 400 °F for two weeks. High temperature aging tests were conducted at 400 °F in order to accelerate the process for thermal strength retrogression in the test specimens in a short period of time. Compressive strength measurements of specimens first cured at 140 °F for three days, and then aged at 400 °F, were used for evaluation. A major screening criterion was that a high temperature HTC-Mix formulation should

have a minimum compressive strength of 800 psi after aging at 400 °F for two weeks and otherwise have good rheological properties and normal setting behaviour at 140 °F.

As shown in Table 2, C-56, C-57 and other formulations met the selection criteria. Both C-56 and C-57 had compressive strengths greater than 800 psi after aging at 400 °F for two weeks. C-56 utilized ground glass, while C-57 used "NEWCEM" (commercial granulated blast furnace slag from Blue Circle Cement Company). C-57 formulation was designated as HTC-Mix and more testing was conducted.

The C-57 (HTC-Mix) slurries were cured at 140 °F, and cores were tested for Brinell hardness and crushed for compressive strength. The results are given in Table 3. There were no problems with slurry rheologies even at higher concentrations. Strength development is also excellent at this temperature.

C-57 is the most suitable formulation for the HTC-Mix composition. Both C-56 and C-62 formulations would be more expensive than C-57 due to higher material costs of ground glass and MC-100. The powdered glass is not commercially available at this time. MC-100 is a slag which is specially ground to ultra fine particle sizes.

TABLE 2 Compressive strengths of HTC-Mix formulations at 300 lb/bbl in 9.5 lb/gal laboratory Diatomite mud after heat aging at 400 °F for two weeks.

Formulation Component	C-56B	C-57C	C-60	C-61	C-62
	Composition (wt%)				
Class A Cement	59	33	33	50	33
"SS-C200"	14	17	17	14	17
"DIAMIX A"*	--	14	14	--	14
Flyash, Type F	--	--	--	--	--
Ground Glass	24	--	33	33	--
"NEWCEM"	--	33	--	--	--
"MC-100"	--	--	--	--	33
Na_2CO_3	3	3	3	3	3
Compr. Strength (psi)	850	1020	405	880	1000

Formulation Component	C-63[1]	C-64	C-65	C-66	C-68[1]
	Composition (wt%)				
Class A Cement	33	33	32	33	33
"SS-C200"	16	17	17	17	17
"DIAMIX A"*	14	14	--	--	--
Flyash, Type F	--	--	--	14	--
Ground Glass	--	--	--	--	--
"NEWCEM"	17	23	48	33	47
"MC-100"	17	10	--	--	--
Na_2CO_3	3	3	3	3	3
Compr. Strength (psi)	910	810	625	930	700

*"DIAMIX A" is Type N mined natural pozzolana by BJ Corporation.

[1] A C-57 equivalent.

TABLE 3 Compressive strengths of C-57 samples cured at 140 °F at varying concentrations for a laboratory Diatomite mud treated with 8 lb/bbl SPERSENE.

C-57 Concentration (lb/bbl)	Compressive Strength (psi) UCA*	UCA* Core Crushed	Brinell Hardness
350	2 369	3 060	3 341
300	1 874	1 365**	2 664
230	1 593	1 660	2 209
200	1 073	1 690	1 671

*Ultrasonic Cement Analyzer by Halliburton.
**Sample was defective.

Table 3 demonstrates the effect of C-57 concentration on compressive strength. A 9.5 lb/gal lab Diatomite mud treated with 8 lb/bbl "SPERCENE CF" was used for the mud conversion. The higher the C-57 concentration, the stronger the cement becomes. In general, API compressive strengths or equivalent crushed compressive strength values of an HTC-Mix or S-Mix are about 1.5 times higher than the corresponding UCA compressive strengths.

A series of long-term exposure tests were conducted on C-57 slurries at 300 lb/bbl in a laboratory prepared Diatomite mud treated with 8 lb/bbl "SPERCENE CF" (MI Drilling Fluids lignosulphonate mud thinner). The HTC-Mix slurries were poured into two 2-inch cubic brass molds and cured in a high temperature curing chamber which was programmed to maintain 140 °F for three days and then ramped up to and held at 400 °F for a specified period of time. All high temperature strength data represent an average of two cubes. As shown in Table 4, the aging time was varied from half day to six months. Obviously, one half day is not enough to cause complete strength retrogression at 400 °F. However, the compressive

strength of C-57 was fairly constant up to six months after initial strength reduction shown in two-week tests.

TABLE 4 Long term compressive strength monitoring of 300 lb/bbl C-57 at 400 °F.

Exposure Time	Compressive Strength (psi)	Number of Samples
0.5 day	1 890	2
2 weeks	960	14
1 month	950	4
2 months	970	2
3 months	810	2
6 months	830	2

An effort was made to determine an exact amount of chrome-free lignosulphonate thinner needed for an acceptable thickening time of five to eight hours at a BHCT (bottom hole circulation temperature) of 107 °F. The effect of chrome-free lignosulphonate thinner concentration on thickening time of an HTC-Mix slurry prepared with 200 lb/bbl C-57 in a 9.5 lb/gal lab Diatomite mud was measured. The C-57 was dry blended using a standard C-57 formulation comprising 33% Riverside Class G cement, 17% "SS-C200" (sodium silicate made by PQ Corporation), 14% Bakersfield "POZMIX A" (flyash supplied by Halliburton), 3% soda ash, and 33% "NEWCEM" (blast furnace slag made by Blue Circle Cement Company). Thickening times were measured on an Autoclave Consistometer at a BHCT of 107 °F (heating rate 1.83 °F/min) and at 2 000 psi. Table 5 lists "SPERCENE CF" concentrations and resulting thickening times of this HTC-Mix slurry.

TABLE 5 Thickening time versus "SPERCENE CF" concentration with a 200 lb/bbl C-57 in 9.5 lb/gal Diatomite mud.

"SPERCENE CF"* Concentration (lb/bbl)	Thickening Time at 107 °F (Hr:Min)
2.00	2:08
2.10	2:46
2.15	2:50
2.20	7:32
2.25	14:37
2.50	17:36
3.00	16:44
3.00 + 20 lb/bbl Gel	1:42
5.00 + 20 lb/bbl Gel	18:45

*Chrome-free lignosulphonate made by MI Drilling Fluids.

Table 5 indicates that "SPERCENE CF" is a powerful retarder for this HTC-Mix slurry and the thickening time is very sensitive to the concentration of SPERSENE CF. An optimum concentration is 2.2 lb/bbl under this test condition. In order to check the sensitivity of "SPERCENE CF" concentration on thickening time, 20 lb/bbl bentonite was added to an HTC-Mix slurry containing 3 lb/bbl "SPERCENE CF". The thickening time was reduced from 16:44 to 1:42 due to the addition of gel. An addition of an extra amount of 2 lb/bbl "SPERCENE CF" to this slurry has brought the thickening time back to the original level.

In Table 6, the effect of "UNICAL CF" on the compressive strength development of C-57 slurry consisting of 9.1 lb/gal Diatomite field mud treated with 200 lb/bbl C-57 is shown. The higher the "UNICAL CF" concentration, the stronger the HTC-Mix becomes. There is no appreciable difference in rheology; there are

dramatic differences in set strengths. UCA and API compressive strengths increase proportionally with the concentration of "UNICAL CF".

TABLE 6 Effect of "UNICAL CF", a chrome-free lignosulphonate made by Milpark, on rheology and compressive strength of a 200 lb/bbl C-57 in 9.1 lb/gal Diatomite mud.

"UNICAL CF" Concentration (lb/bbl)	Rheology (PV/YP)	UCA Compressive Strength (psi)	UCA Core Crushed Strength (psi)	UCA Set Time @ 500 psi (hr:min)
2.2	12/15	447	630	5:36*
6.0	20/2	644	1 060	9:00
8.0	13/6	733	1 400	8:29
10.0	14/4	888	1 540	9:32
12.0	13/3	984	2 070	8:34

PV - plastic viscosity, cp
YP - yield point, lb/100 ft^2.
Mud - 9.05 lb/gal field mud from well 523-29 treated with 10.8 lb/bbl sodium chloride.

*Time to reach at 447 psi.

The yield and density of HTC-Mix is calculates as follows. A "yield" value in cubic feet/sack of a slurry to be mixed must be entered to operate an automatic density control unit installed on some cement mixing units. As in any other cement calculations, a specific gravity and a bulk density are needed to calculate a yield value of HTC-Mix. Therefore, specific gravities and bulk densities of individual ingredients along with the C-57 HTC-Mix formulation are given in Table 7.

TABLE 7 C-57 formulation and specific gravity (s.g.) and bulk density (b.d. in lb/ft^3) values.

C-57 Component	Percent	s.g.	b.d.
Class G Cement	33	3.14	94
"SSC-200"	17	2.478	74
"POZMIX A"	14	2.468	74
Soda Ash	3	2.533	76 (?)
Slag	33	2.90	86.5
Composite Value	100	2.84	84.79

The calculated bulk density of the C-57 formulation is approximately 85 pounds/cubic foot which was verified to be reasonable in the laboratory. The calculated specific gravity is 2.84 which was experimentally confirmed to be accurate.

A water flood injector well, 567-GR-29, and a producer well, 523-29 were cemented with HTC-Mix. These wells are located in the South Belridge Field, California.

An 11.5 lb/gal HTC-Mix was pumped as the lead slurry which was designed to fill the 7-inch annulus from 200 feet from the TD for (3 000 feet) both Diatomite wells. The HTC-Mix, tail, and cap cements were dry blended at the service company bulk plant.

The HTC-Mix was mixed at 200 lb/bbl in a 9.05 lb/gal mud and pumped using the same equipment as a standard job with the exception of using drilling mud instead of water to mix cement. A "slotted pump shoe" was placed in the suction compartment of the mud pit to filter out drill cuttings which might otherwise plug up the cementing equipment. A portable centrifugal pump was used to pump the mud from the mud pit to the RCM cement mixing unit. All slurries were mixed and pumped "on the fly" using the RCM cement unit which was manually operated.

A 15.6 lb/gal tail slurry consisting of Class H, 35% "SSA-1" (silica flour supplied by Halliburton) and 3% $CaCl_2$ was pumped to fill the bottom 200 feet. A small volume of 15.6 lb/gal cap slurry

consisting of Class H cement, 35% SSA-1, 3% $CaCl_2$, and a 10-pound sack of "CAL-SEAL" (calcium sulphate hemahydrate supplied by Halliburton) were also pumped down in the annulus at the completion of pumping the lead and tail cements. The cement designs were the same for both wells. Both cement jobs were placed successfully. An evaluation of these wells by cement bond logs, "CBT" (Cement Bond Tool by Schlumberger) and "CET" (Cement Evaluation Tool by Schlumberger) was very good.

Three special geophone wells were drilled and completed in the South Belridge field. A geophone assembly is 2.2 inches OD, 11 inches long, and connected to 150 pairs of twisted wire in 1/2-inch OD cable. An array of 50 geophones spaced every 5 feet for high-resolution tomography over a 250-feet interval was strapped on a 2-7/8-inch tubing. The tubing strapped with the geophone assemblies was used to place the geophones at a proper location in the wellbore and to pump cement through the tubing.

It was extremely critical for the success of the project to properly cement these geophone assemblies. In order to provide maximum acoustic transmission, a good bond as well as absence of any mud or air pockets in the wellbore were necessary. A low viscosity slurry was needed in order to completely fill all gaps and to cover irregularly shaped geophones.

For the purpose of logging these wells, a non-dispersed "NEWDRILL" (Milpark's partially hydrolyzed polyacrylamide polymer) mud was treated with sodium chloride to maintain a filtrate salinity from 18 000 to 20 000 ppm chloride for the first geophone well. Potassium chloride was used for the second and third geophone wells. The mud was treated with a higher level of lignosulphonate thinner in order to reduce the slurry viscosity and to provide higher compressive strengths. The type of salt used in the mud system and concentration of lignosulphonate thinner are as follows:

Geophone Well ID	Type of Salt Used in Mud	Lignosulphonate Thinner Concen-centration (lb/bbl)
#1	NaCl	6.0
#2	KCl	6.0
#3	KCl	4.0

HTC-Mix was dry blended. For each well, a total of 45 757 pounds of final blend containing 44 400 pounds of C-57 and 1 333 pounds of lignosulphonate (6 lb/bbl in mud) was prepared. The HTC-Mix was mixed with 9.05 lb/gal mud at a ratio of 200 pounds C-57 per barrel of mud. A total of 267 barrels HTC-Mix was pumped by mixing the dry blend into 222 barrels of the mud.

The HTC-Mix slurry was pumped at approximately 4 bpm (barrel per minute). A 25-sacks tail slurry was pumped to cover the casing shoe. This cementing procedure was used for all three geophone wells.

Mud densities for all three geophone wells were 9.05 lb/gal. The sample densities seem to be more uniform and slightly higher than the densometer readings.

All three HTC-Mix slurries were very thin. All the Fann 35 Viscometer 6 rpm and 3 rpm readings were zero. Plastic viscosities were low and yield point values were close to zero or less than zero. Although the 3-second gels were close to zero, 10-minute gels were much higher than the 3-second gels.

The success of cementing operations and the quality of cement jobs were evaluated by microseismic minifracture experiments. Signals from discrete microseismic events were excellent in all three observation wells.

The following examples relate to S-Mix.

S-Mix is formulated with blast furnace slag and common alkaline activators. S-Mix formulations were field tested in two Diatomite wells, 514L-29 and 568E-33, in the Belridge Field,

California, and in a North Hobbs Unit well, 27-221W, in Hobbs, New Mexico. All cementing operations were successfully carried out.

A series of UCA strength development experiments was carried out by adding 225 lb/bbl Colton ground slag to a 9.8 lb/gal polymer mud (0.94 bbl water, 12 lb/bbl bentonite, 0.1 gal/bbl partially hydrolyzed polyacrylamide, 0.25 lb/bbl carboxymethylcellulose, 60 lb/bbl slag, 35 lb/bbl "REVDUST", simulated drill solids by Milwhite) and by treating the resulting slurry with varying amounts of activators and thinners. A representative S-Mix formulation (225 lb/bbl slag, 9 lb/bbl NaOH, 3 lb/bbl Na_2CO_3, and 4 lb/bbl "MILTEMP", sulphonated styrene maleic anhydride copolymer from Milpark) was used for a full-scale displacement test. This S-Mix formulation had the following properties:

Plastic Viscosity, cp	19
Yield Point, lb/100 ft^2	34
10-sec Gel Strength, lb/100 ft^2	16
10-min Gel Strength, lb/100 ft^2	32
Thickening Time at 120 °F, hr:min	4:42
API Fluid Loss, 80 °F/100 psi, ml	31.4
Cement Fluid Loss, 120 °F/1000 psi, ml	106
API Free Water, ml	0
API Compressive Strength, psi	1 531
(Aged at 140 °F/7 days, average of 6 samples)	
Shear Bond, psi	59
(Aged at 140 °F/7 days, average of 4 samples)	

A 9.3 lb/gal PetroDrill (PHPA, partially hydrolyzed polyacrylamide, shale-controlling agent from UniBar) mud was converted into an 11.8 lb/gal S-Mix slurry by adding 165 lb/bbl Colton ground slag and 2 lb/bbl Miltemp (SSMA) as a thinner and retarder.

For each Diatomite well, a total of 17 900 lb of S-Mix was dry blended at the service company yard. The formulation for the S-Mix and actual weights for each ingredient are as follows:

Colton Slag	165 lb/bbl	16 500 lb
Caustic Soda Bead	9 lb/bbl	900 lb
Soda Ash	3 lb/bbl	300 lb
SSMA*	2 lb/bbl	200 lb

* sulphonated styrene maleic-anhydride copolymer by Milchem)

This formulation gives a yield of 3.248 cu ft/sack which is equivalent to a volume increase of 16.2 percent. Both S-Mix cementing jobs went well operationally. Both wells had full cement returns.

Prior to the field test of the North Hobbs Unit well, six S-Mix formulations were tested using a 10.45 lb/gal salt saturated mud on UCAs and these test results are tabulated in Table 8. The compressive strengths are reasonable despite the salt-saturated muds and low test temperatures. The UCA compressive strength plots indicate that SS-35 and SS-36 had the shortest set times (4 hr:15 min and 9:03, respectively), while SS-31 and SS-34 had the highest UCA compressive strengths (1 259 psi and 1 187 psi, respectively).

TABLE 8 Effect of activators on UCA set time, UCA compressive strength (C.S) and crushed compressive strength (C.C.S.) of S-Mix in a 10.45 lb/gal salt-saturated field mud.

Sample Number	NaOH (lb/bbl)	Na_2CO_3 (lb/bbl)	Desco CF	Test Temp. (°F)	UCA* Set Time (Hr:Min)	C.S. (psi)	C.C.S. (psi)
SS-31	10	14	-	68	21:33	1 250[1]	1 450
SS-32	10	12	-	68	16.32	1 086[1]	1 550
SS-33	10	10	-	68	15:28	1 094[1]	1 360
SS-34	10	8	-	66	18:20	1 187[1]	1 630
SS-35	10	8	0.25	90	9:03	4032	-
SS-36	10	10	0.25	90	4:15	338[2]	-

*UCA set time to reach a compressive strength of 50 psi, hr:min.
[1]@ 16 days
2@ 1 day
All formulations contain 225 lb/bbl Colton ground slag.

Rheology of	SS-35	SS-36
Plastic Viscosity, cp	21	22
Yield Point, lb/100 ft^2	13	3
Gel Strengths, lb/100 ft^2	8/58	2/8

The SS-36 formulation was chosen because of its faster UCA set time and good rheological properties. A volume of 265 bbl of 10.45 lb/gal salt-saturated mud were converted to 320 bbl of 13.06 lb/gal S-Mix by adding a dry blend of 225 lb/bbl Colton ground slag, 10 lb/bbl soda ash, 10 lb/bbl caustic soda beads, and 0.25 lb/bbl Desco CF (a chrome-free polyphenolic tannin mud thinner). It was dry blended in three approximately equal batches at the Service camp and transported to the well site. The blend was mixed with the field mud, 10.45 lb/gal salt-saturated, and pumped at a rate of 10 barrels per minute using an RCM cement unit. The 5.5-inch long string (4 395 feet TVD) was cemented in this way with this 13 lb/

gal S-Mix lead and a 15 lb/gal conventional tail cement. (This well is a 26° directional well.) All aspects of the cementing operation went well except that the cement mixing operator had some difficulty maintaining a slurry density of 13 lb/gal.

While the slurry compositions methods of use of the invention have been described, many other variations will occur to those skilled in the art. It is intended that all such variations which fall with the scope of the appended claims be embraced thereby.

C L A I M S

1. A method of cementing a well comprising

preparing a mud-cement by admixing (a) a drilling mud, and (b) blast furnace slag and/or particulate glass;

displacing the mud-cement to a preselected location in the well; and

allowing the mud-cement to harden and set up.

2. The method according to claim 1, further comprising admixing to the drilling mud a C-Mix, the amount of C-Mix being between 40 and 90 %wt of the total amount of blast furnace slag, powdered glass and C-Mix.

3. The method according to claim 1 or 2, further comprising admixing to the cement mixture an activator functional to cause the mud-cement to set up.

4. The method according to claim 3, wherein the activator is selected from the group consisting of sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium sulphate, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, and mixtures thereof.

5. The method according to claim 3 or 4, wherein the activator content is from 5 to 35% by weight of the total admixture.

6. The method according to any one of the claims 1-5, further comprising admixing to the drilling mud a thinner or retarder selected from the group consisting of lignosulphonate, lignite, sulphonated lignite, sulfomethylated humic acid, sulphonated styrene maleic-anhydride copolymer, polyacrylate-polyamide co-polymer, organic acids, and mixtures thereof.

7. The method according to anyone of the claims 1-6, further comprising admixing to the mud-cement a material selected from the group consisting of chrome-free lignosulphonate, chrome-free de-sugared lignosulphonate, chrome-free sulfomethylated tree bark

extract, and mixtures thereof to control viscosity and thickening time and to increase strength development of the mud-cement.

8. The method according to any one of the claims 1-7, wherein the drilling mud is selected from the group consisting of water-base mud, seawater mud, salt water mud, brine mud, gypsum mud, lime mud, polymer mud, nondispersed mud, polyalcohol mud, oil-in-water emulsion mud, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 92/00922

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C04B28/08; C04B28/04; E21B33/13

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C04B ; E21B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
P,X	US,A,5 058 679 (A.H. HALE ET AL) 22 October 1991 see column 1, line 19 - line 45 see column 2, line 51 - column 3, line 29 see column 4, line 3 - line 32 see column 15, line 43 - line 65; claims 1-3,5-6; table 2 ---	1,4-6,8
X	US,A,3 168 139 (H. T. KENNEDY ET AL) 2 February 1965 see column 1, line 1 - line 53 see column 2, line 58 - column 3, line 19 see column 12, line 34 - line 68; examples 1,4-5 see claims 1-4	1,3,6,8
Y	---	4,7

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° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
18 AUGUST 1992	27. 08. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	OLSSON S.A.

1

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	FR,A,2 615 183 (M. ROUSSEL ET AL) 18 November 1988 see abstract; claims 1-2 see page 1, line 1 - line 30 see page 2, line 5 - line 24 see page 3, line 12 - line 14 see page 5, line 5 - line 11	4
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Y	GB,A,2 078 280 (GEORGIA-PACIFIC CORPORATION) 6 January 1982 see abstract; claim 1 see page 1, line 7 - line 44 see examples 1,7	7
X	US,A,3 499 491 (E.W. REECE ET AL) 10 March 1970 cited in the application see abstract; claims 1-2,4-9; tables 1-2 see column 3, line 50 - column 4, line 51 see column 6, line 51 - column 7, line 9	1-4,6,8
A	CHEMICAL ABSTRACTS, vol. 104, no. 13, 13 January 1986, Columbus, Ohio, US; abstract no. 9858J, 'Injection compositions for insertion holes of piles' page 263 ; see abstract	1-3

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9200922 SA 58944

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The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82